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REACTION OF BERYLLIUM CERAMIC CRUCIBLES WITH RARE-EARTH METAL MELTS

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Intense chemical reaction of beryllium ceramic crucibles with alloys of metals containing *f*-elements is established using optical absorption spectra, PCL, x-ray diffraction, x-ray-photoelectron spectroscopy, and electron probe in inert and reducing atmospheres (at high temperatures). Beryllium oxide in the diffusion zone is occasionally reduced to the metallic state, which leads to the destruction of ceramic crucible walls. This restricts the use of the specified crucibles in melting alloys containing rare-earth metals.

Ceramics based on beryllium oxide have unique physicochemical properties combining high chemical, thermal, and radiation resistance and high thermal conductivity. Beryllium ceramics articles produced using the traditional technology (semidry molding or slip casting) are widely applied in specialized metallurgy, laser technology, dosimetry, ionizing radiation, and electronics.

Beneficial physicochemical properties make it possible to use beryllium ceramic products as efficient refractories. It is known that crucibles made of such ceramics are used for melting rare and precious metals when especially pure metals or alloys are required. The working temperature of such crucibles may reach 2000°C. Due to the high melting temperature (about 2550°C) [1], thermal and chemical resistance, and purity, beryllium ceramics crucibles are used to melt uranium and plutonium. Such crucibles are successfully used to produce standard samples of silver, gold, and platinum.

Of special interest is the interaction of beryllium ceramic crucibles with metal melts containing impurities of *f*-elements. The high transparency of such ceramics to SHF-radiation allows for using such crucibles in furnaces with induction heating.

Attempts to obtain metal melts containing impurities of rare-earth metals (REM) in crucibles made of beryllium ceramics (in furnaces with SHF heating) in inert and air atmospheres as a rule ended with the crucible burning through and the melt spilling outside.

Therefore, the study of the mechanism of the reaction of *f*-elements with ceramics based on beryllium oxide at high temperatures, as a consequence of which the crucibles are destroyed, is of practical significance.

In studying the temperature dependence of the viscosity of metal melts containing 0.1 – 0.5 wt.% of cerium impurities in helium (at a temperature up to 1700°C) and other inert gases, hysteresis was discovered in the melt viscosity polytherms. The amount of the melt in the crucibles decreased, and the beryllium ceramic crucibles became impregnated with melted metal and acquired a yellow-gray color. To study the phenomena, thin plates (0.5 – 1.0 mm) where cut out of the crucibles and subjected to grinding and polishing. Beryllium ceramics in the course of alloy melting was significantly compacted, which made it possible to study the absorption and cathode luminescence spectra and to identify the impurity phase.

The absorption spectra of samples were studied using a Specord M-40 spectrophotometer at room temperature within a spectra range of 200 – 800 nm (Fig. 1*a*). The presence of several intense absorption bands is registered in the ultraviolet and violet-blue spectrum ranges, which correlates with the allowed transitions $4f – 5d$ in the ion Ce^{3+}. It is known [2 – 4] that the 4*f*-shell of Ce^{3+} ion contains one electron, which may exist in the main state $^2F_{5/2}$ or in the state $^2F_{7/2}$. The transitions of electrons from level $4f$ to a lower split level $5d$ determine the optical absorption spectrum of Ce^{3+} ion in the UV spectrum range.

The samples of beryllium ceramics with a cerium impurity at room temperature exhibit several absorption bands within the spectral range of 200 – 415 nm: an intense complex band consisting of at least two overlapping peaks with maxima at 301 and 318 nm and a weaker band at 370 nm, which is due to the transitions between the levels $4f – 5d$ of the ion Ce^{3+} [4]. The existence of several wide absorption bands is presumably related as well to some specifics of splitting of the *d*-shell of the Ce^{3+} ion in the crystalline field of the BeO lattice. The most intense maximum at 250 nm in the UV spectrum range correlates with absorption of Ce^{4+} ion. It is believed that Ce^{4+} ions are not capable of lumines-

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cence and impart the characteristic yellowish tint to beryllium ceramics. The high intensity of the band at 250 nm is presumably related to an increased concentration of Ce^{4+} ions, i.e., with the existence of the CeO_2 phase.

Thus, the optical absorption spectra show the existence of impurity cerium ions of different valence in ceramics taken from the crucible walls. The existence of Ce^{3+} impurity is corroborated as well by the data on pulse cathode luminescence (PCL) spectra of the same samples (Fig. 1*b*).

The PCL was measured (at the Institute of Electronics of the Ural Branch of the Russian Academy of Sciences) at room temperature on an experimental plant, in which the source was a RADAN-220 electron accelerator with energy up to 200 keV. The maximum electron current reached 2 kA with the constant excitation pulse duration equal to 2 nsec. The PCL spectra of beryllium ceramic crucible in the UV spectra range consisted of three overlapping peaks with maxima at 295, 324, and 339 nm correlating with the luminescence of Ce^{3+} ions. The luminescence of the peak at 295 nm is strongly influenced by more intense natural luminescence of ceramics, whose luminescence maximum lies near 250 nm.

An analysis of x-ray patterns of beryllium ceramics (non-impregnated and impregnated with cerium melt) indicated an expansion and a shift of the reflections of some crystallographic planes, which probably points to a possible dissolution of a part of the cerium impurity in the crystal lattice of BeO. The analysis also registered splitting of the reflection with $d = 2.190$ of crystallographic plane (002), the emergence of new weak reflections with interplanar distances $d = 2.6650, 1.8835, 1,6884,$ and 1.5470, as well as variations in the relative intensity of reflections of crystallographic planes (101) and (100). This may indicate the presence of the impurity phase on the surface of BeO microcrystals and pores.

Attempts to obtain metal alloy using other *f*-elements (for instance, alloys based on Fe, B, Co with impurities of Nd and Tb and Co with Sm) in beryllium ceramic crucibles (in inert and air atmospheres) in SHF resistance furnaces at temperatures at $1500 – 1700°C$ containing from 1 to a few percent of REM always ended with the destruction of the crucible walls and the melt flowing outside.

The diffusion zone on the site of destruction of beryllium ceramic crucibles was studied using a Camebax electron scanning probe on secondary electrons and characteristic radiation and it was found that from a melt consisting of Fe, B, and Co with Nd and Tb impurities, only the said impurities diffused into the crucible in a reliably significant amount. The other components remained in the melt.

The diffusion zone of Sm – Co alloy on the crucible wall surface made of beryllium ceramics was studied using a scanning electron probe. The conducting phase correlating with the metallic phase has a light color in the secondary electrons. The ceramic phase, into which the impurity atoms diffuse, has lower electric conductivity and is dark-colored. It is mostly the samarium impurity that diffuses into the crucible material in the characteristic $Sm_{\alpha\alpha1}$ radiation.
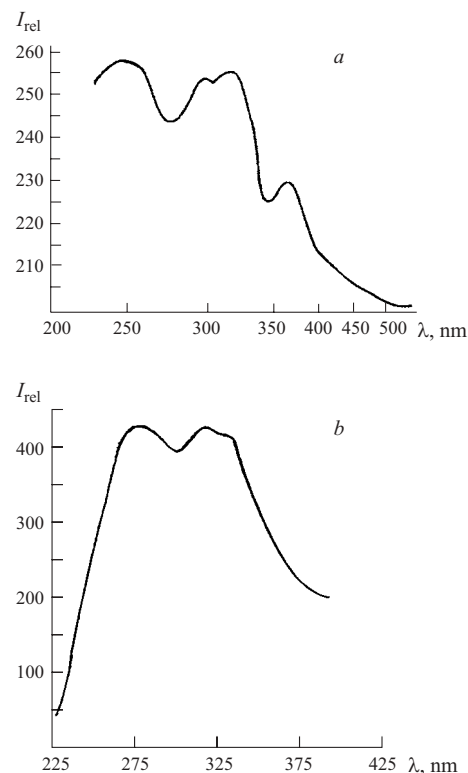

Fig. 1. Absorption (*a*) and PCL (*b*) spectra of beryllium ceramics with cerium impurities at room temperature.

REMs have stronger chemical affinity to oxygen than beryllium; therefore, REM ions are able to take oxygen from Be^{2+} ions and reduce beryllium in ceramics. This is also substantiated by the results of studying the diffusion zone on an ESCA-3 x-ray-photoelectron spectrometer in a vacuum of 10^{-9} mbar.

The precision of identifying the bond energy of the electron levels was ± 0.1 eV. Charging of the samples was accounted for with respect to the electron level peak C1s with a bond energy of 284.6 eV, which is present in the spectrum and weakly changes its position on the energy scale (depending on additional charging of the samples) and presumably correlates with the impurity phase of beryllium carbide Be_2C $(1 – 2$ wt. %). The surface of the diffusion zone was purified from hydrocarbon contaminations by bombardment with Ar^+ ions. The position of the electron level Be1s on the energy scale was studied. Ceramic samples cut out of the walls of another crucible of the same batch, in which no metal had been melted, were used for reference purposes. It is found that the bond energy of the electron level Be1s in the reference samples varies within a range of $113.3 – 113.7$ eV, whereas the same energy in the diffusion zone varies in the range of $112.3 – 112.6$ eV. A decrease in the bond energy of the electron level Be1s (by approximately 1 eV) points to partial destruction of beryllium on the ceramic surface [5].

Thus, the destruction of beryllium ceramic crucibles in contact with melts containing *f*-element impurities is due to

the fact that BeO at high temperatures reacts with REM and results in the formation of their oxides. This happens most intensely in the presence of an oxygen-free (inert or reducing) atmosphere. BeO in the liquid state reacts with REM according to the following reaction:

$$2M + 3BeO = M_2O_3 + 3Be,$$
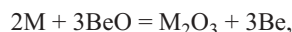
where M is REM, with the formation of a certain quantity of metal beryllium having a melting point of about 1284°C. When the temperature of REM alloys with other metals exceeds 1500 – 1600°C, the walls of beryllium ceramic crucibles become destroyed.

Beryllium oxide (with molar content of $10^{-4} - 10^{-5}$ %) has a low isomorphic capacity for impurities [1]. The majority of the REM impurities do not incorporate isomorphically into the crystal lattice of BeO and are located along the boundaries of BeO microcrystals and pores. Only a rather small part of REM ions is probably able to occupy predominantly the octahedral voids in the packed hexagonal crystal lattice of BeO. The incorporation of a part of the *f*-element impurities into the positions of Be^{2+} ions in the oxygen tetrahedron appears doubtful due to the significantly larger REM ion radii compared with Be^{2+} (0.034 nm).

The reactions of REM with oxygen at the site of contact with beryllium ceramics is accompanied by the formation of oxygen vacancies in the anion sublattice of BeO. The surface state of beryllium and REM atoms in this case can be presumably represented by the scheme Be – O – REM [6]. A quasi-anion vacancy is formed near the ion Be^{2+}. Its energy spectrum differs insignificantly from that of a typical anion vacancy, which is inherent only in BeO. This vacancy has increased resistance to such processes as diffusion (it is firmly localized) and annihilation due to its rigid coordination by the REM ions.

Thus, intense chemical reaction of beryllium ceramic crucibles with metal melts containing *f*-elements was established using optical; absorption spectra PCL, x-ray diffraction analysis, x-ray-photoelectron spectroscopy, and electron probe in inert and reducing atmospheres (at high temperatures).

Beryllium oxide in the diffusion zone is occasionally reduced to the metallic state, which leads to the destruction of ceramic crucible walls. This limits the use of the specified crucibles for melting alloys containing REM.

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